Memorandum

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Subject: Effects Determination for Molinate and Thiobencarb for Pacific Anadromous Salmonids

Summary

I reviewed data and other information for molinate, a pesticide named by the Californians for Alternatives to Toxics (CATs) and thiobencarb, a pesticide named by the Washington Toxics Coalition (WTC). It makes sense to consider these two pesticides together because they are both thiocarbamate herbicides used on rice. Although thiobencarb is also registered for use on lettuce, endive, and celery in Florida only, and both herbicides are used on rice in the southeastern U. S., the only overlap between these two herbicides and salmon and steelhead occurs in California. I conclude based on the considerations below and in the attached and/or referenced materials that these two herbicides registered for use on rice are not likely to adversely affect Federally listed threatened and endangered salmon and steelhead, nor are they likely to adversely modify their designated critical habitat.

Actually, it appears most likely that these two pesticides will have no effect on salmon and steelhead. However, they do exhibit some fish toxicity and they are used in areas in the vicinity of salmon and steelhead. California's Department of Pesticide Regulation has taken steps to markedly reduce the concentrations of these two pesticides so that they are well below our criteria of concern in natural waters based upon extensive monitoring studies.

Background

Under section 7 of the Endangered Species Act, the Office of Pesticide Programs (OPP) is required to consult on actions that 'may affect' listed species or that may adversely modify designated critical habitat. Situations where a pesticide may affect a fish, such as any of the salmonid species listed by the National Marine Fisheries Service, include either direct or indirect effects on the fish. Direct effects result from exposure to a pesticide at levels that may cause harm. Relevant acute data are derived from standardized toxicity tests with lethality as the primary endpoint. These tests are conducted with what is generally accepted as the most sensitive life stage of fish, i.e., very young fish from 0.5-5 grams in weight, and with species that are usually among the most sensitive. These tests for pesticide registration include analysis of observable sublethal effects as well. Typically, a standard fish acute test will include concentrations that cause no mortality, and often no observable sublethal effects, as well as concentrations that would cause 100% mortality. By looking at the effects at various test concentrations, a dose-response curve can be derived, and one can statistically predict the effects likely to occur at various pesticide concentrations; a well done test can even be extrapolated to concentrations below those tested (or above the test concentrations if the highest concentration did not produce 100% mortality)[1].

OPP evaluates the potential chronic effects of a pesticide on the basis of several types of tests. These tests are often required, but not always. If a pesticide has essentially no acute toxicity at relevant concentrations, or if it degrades very rapidly in water, or if the nature of the use is such that the pesticide will not reach water, then chronic fish tests may not be required. Chronic fish tests primarily evaluate the potential for reproductive effects and effects on the offspring. Other observed sublethal effects are also required to be reported. An abbreviated chronic test, the fish early-life stage test, is usually the first chronic test conducted and will indicate the likelihood of reproductive or chronic effects at relevant concentrations. If such effects are found, then a full fish life-cycle test will be conducted. If the nature of the chemical is such that reproductive effects are expected, the abbreviated test may be skipped in favor of the full life-cycle test. These chronic tests are designed to determine a "no observable effect level" (NOEL) and a "lowest observable effect level" (LOEL).

An analysis of toxicity, whether acute or chronic, must be combined with an analysis of how much will be in the water, for fish. Risk is a combination of exposure and toxicity. Even a very highly toxic chemical will not pose a risk if there is no exposure, or very minimal exposure relative to the toxicity. OPP uses a variety of chemical fate and transport data to develop "estimated environmental concentrations" (EECs) from a suite of established models. The acute or chronic EEC is compared with the acute or chronic toxicity, respectively, to determine if there is risk. Generous safety margins are used for both acute risk and for chronic risk in rivers and streams. For ponds, there is still a reasonable safety margin for chronic risk, but it is not "generous". While our risk assessment criteria are intended to protect populations of non-target species that are not listed as endangered or threatened, our criteria (levels of concern) for

endangered and threatened species are intended to protect individuals of these species from not only lethal effects, but also sublethal, reproductive, and chronic effects.

We also attempt to protect listed species from indirect effects of pesticides. We note that there is not a clear distinction between indirect effects on a listed species and adverse modification of critical habitat (discussed below). By considering indirect effects first, we can provide appropriate protection to listed species even where critical habitat has not been designated. In the case of fish, the indirect concerns are for food and cover. In general, pesticides applied in terrestrial environments will not affect the plant material in the water that provides aquatic cover for listed fish. Thus the primary indirect effect of concern would be for the food source for listed fish. However, it is not necessary to protect individual organisms that serve as food for listed fish. Thus, our goal is to ensure that pesticides will not impair populations of these food organisms. For fish, this is primarily for aquatic invertebrates, although aquatic plants or plankton may be relevant food for some fish species. We already are protecting food fish at the individual level because we are protecting the listed fish at the individual level, so there is nothing extra we need to do to ensure an adequate supply of fish as food of listed fish. As you know, comparative toxicology has demonstrated that various species of scaled fish generally have equivalent sensitivity, within an order of magnitude, to other species of scaled fish tested under the same conditions.

OPP is also required to consult if a pesticide may adversely modify designated critical habitat. We consider that the use of pesticides on land could have such an effect in a few circumstances. For example, use of herbicides in riparian areas could affect riparian vegetation, especially woody riparian vegetation, which possibly could be an indirect effect on a listed fish. However, there are very few pesticides that are registered for use on riparian vegetation, and the specific uses that may be of concern have to be analyzed on a pesticide by pesticide basis. In considering the general effects that could occur and that could be a problem for listed salmonids, the primary concern would be for the destruction of vegetation near the stream, particularly vegetation that provides cover or temperature control, or that contributes woody debris to the aquatic environment. Destruction of low growing herbaceous material would be a concern if that destruction resulted in excessive sediment loads getting into the stream, but such increased sediment loads are insignificant from cultivated fields relative to those resulting from the initial cultivation itself. Increased sediment loads from destruction of vegetation could be a concern for uncultivated areas. Any increased pesticide load as a result of destruction of terrestrial herbaceous vegetation would be considered a direct effect and would be addressed through the modeling of estimated environmental concentrations. Such modeling can and does take into account the presence and nature of riparian vegetation on pesticide transport to a body of water.

As you are aware, all of our risk assessment procedures, toxicity test methods, and EEC models have been peer-reviewed by OPP's Science Advisory Panel. The data from toxicity tests and environmental fate and transport studies undergo a stringent review and validation process in accordance with "Standard Evaluation Procedures" published for each type of test.

Analysis

Organization

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3. Brief description of salmon and steelhead Evolutionarily Significant Units that may be exposed
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1. Description of thiobencarb and molinate

Molinate and thiobencarb are both thiocarbamate herbicides that have been subject to the process of reregistration. The thiobencarb Reregistration Eligibility Document (RED) was issued in September, 1997. The chapters for the molinate RED are currently posted on our web site for public comment, which closed on June 3. Most of the information used in the assessments below is derived from the relevant RED. Typically, a RED will indicate if there are risks of concern, i.e., exposure that exceeds a "level of concern" (LOC), where there is one level of concern for "high risk", a second as a trigger for "restricted use classification", and a third, more sensitive level of concern for threatened and endangered species. Of course, these REDs address all kinds of species groups, but rarely deal with particular species; I have attempted to apply the findings of these REDs to the listed salmonids. I have supplemented this with additional information obtained from the U. S. Geological Survey, California Department of Fish and Game, California EPA's Department of Pesticide Regulation, and other sources.

<u>Thiobencarb</u>
Thiobencarb is the common name for S-((4-chlorophenyl)methyl)diethylcarbamothioate. The PC Code used internally is 108401. The Chemical Abstract Services unique identifier for thiobencarb is 28249-77-6. Trade names currently used in the U. S. are Bolero and Abolish.

Thiobencarb is a systemic herbicide that acts through inhibiting shoot development in early seedling growth. While it may control a wide spectrum of weeds (see page 2 of RED), its use in California rice is primarily for control of watergrass, along with sedges and sprangletop, although other weeds are on the label.

Currently, there are five products containing thiobencarb registered under Section 3 of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). They consist of one technical (manufacturing use) product containing 97.4% active ingredient (ai), two emulsifiable concentrate end-use products each containing 84.0% ai, and two granular end-use products each containing 10.0% ai. In addition, there are two Special Local Needs registrations for California that address worker protection but provide nothing additional to the Federal label with respect to fish and wildlife.

Molinate

Molinate is the common name for S-Ethyl hexahydro-1H-azepine-1-carbothioate. The PC Code used internally is 041402. The Chemical Abstract Services unique identifier is 2212-67-1. The trade name for products containing only molinate is Ordram.

Currently, there are ten products containing molinate registered under section 3 of FIFRA. They consist of two technical (manufacturing use) products containing 96% ai, three granular end use formulations containing 15% ai and one emulsifiable concentrate product containing 90.9% ai that contain only molinate. Two other products, Riceco Touche and Arrosolo, contain 33% ai molinate and 33% ai propanil; these products with propanil are not permitted for use in California. In addition, there is a Special Local Needs registration for California; this California registrations is for the purpose of modifying the federal label with respect to pesticide applicators and farm workers. The use of molinate in rice is primarily for the control of watergrass, although other pest plants are on the label.

Use of molinate and thiobencarb in California[2]

Although there is slight variation depending upon weather, application of molinate to 'early' rice begins in early April and continues through late May. Application of thiobencarb begins in mid-April and goes through the end of May. Thiobencarb is considered to yield better control of sprangletop and sedges, while molinate provides better control of watergrass. Most of the Colusa County rice is treated with either thiobencarb or molinate. In Colusa County, about 60 % of the acreage is treated with thiobencarb and about 40% with molinate; only about 5% is treated with both. These percentages may vary somewhat from year to year and among various counties depending upon pest pressure and efficacy considerations. In California, both of these are applied aerially primarily as granular formulations. The emulsifiable concentrate liquid of thiobencarb may be applied aerially or by ground equipment. Although the use of molinate as a liquid spray is registered, it is very rarely used. California's Pesticide Use Reporting database does not distinguish the form of the active ingredient (i.e., granular or emulsifiable concentrate) that is applied, although such information can be obtained by inspecting individual county permits.

2. Rice production and use of thiobencarb and molinate

Rice is a major crop in California, with over 500,000 acres grown in 1997, when the last agricultural census was taken[3]. Most of the rice production is in the Sacramento River Basin in northern California. Only about 16,700 acres of rice are in the San Joaquin River Basin. Tables 1 and 2 present the latest available information on rice, and on molinate and thiobencarb use on rice. For the state, approximately half of the rice acreage is treated with thiobencarb and approximately half is treated with molinate (Table 1). Molinate is fairly specific for control of watergrass; thiobencarb is used for control of sprangletop and sedges, in addition to watergrass.

Table 1. Acreage of rice, from 1997 agricultural census, and use of molinate and thiobencarb reported to the Department of Pesticide Regulation in the year 2000, in California counties			
County	1997 acres	2000 acres treated with molinate (+ pounds ai)[a]	2000 acres treated with thiobencarb (+ pounds ai)[a]
Alameda	684	0	0
Butte	102,410	53,909 (208,774)	48,802 (189,377)
Colusa	129,974	48,128 (162,717)	91,143 (350,122)
Fresno	4771	2170 (6682)	2216 (8866)
Glenn	83,771	43,008 (164,011)	32,336 (154,454)
Madera	353	94 (423)	0
Merced	4341	1993 (7553)	509 (1879)
Placer	16,661	12,179 (48,451)	844 (2305)
Sacramento	8069	3367 (14,608)	5765 (22,506)
San Joaquin	4700	3037 (8047)	245 (978)
Stanislaus	2564	1397 (3752)	0
Sutter	95,382	68,213 (257,016)	45,041 (180,448)
Tehama	723	0	0
Yolo	26,332	13,477 (55,865)	13,568 (54,186)
Yuba	32,914	25,338 (87,887)	11,881 (41,205)
total	513,649	276,310 (1,025,785)	252,350 (1,006,326)

a. The figures in this table for "acres treated" actually indicate "acre treatments". Two applications to the same 40 acre field will be shown as 80 acres treated. Thiobencarb may be applied once, or it may be applied as a split application at half the rate for each application, which would double the apparent acreage being treated, but would not affect the amount applied.

Rice production and herbicide use data have been updated for the Sacramento River Basin counties in a 2001 Rice Pesticides Program review[4]. The planted acreage in 2001 was reduced from the previous year by over 75,000 acres. There was a comparable reduction in the intended use of molinate and thiobencarb, both of which were reduced by over 50,000 acres in areas treated. "Intended" use (Table 2) is based upon the required requests for permits from the county agricultural commissioners. Actual use data for 2001 are not yet available.

Table 2. Acreage of rice planted in northern California, and amount of molinate and thiobencarb for which permits were requested from county agricultural commissioners for 2001			
County	2001 acres	2001 acres intended to be treated with molinate	2000 acres intended to be treated with thiobencarb
Butte	90,000	42,089	40,239
Colusa	118,000	42,862	63,071
Glenn	84,330	39,598	32,934
Placer	15,700	8,524	988
Sacramento	9700	945	5,554
Sutter	104,722	50,183	21,621
Tehama[a]	1000	0	0
Yolo	35,546	7,209	13,520
Yuba	35,132	24,664	2,515
total	494,130	217,250	181,037

a. The rice grown in Tehama County is organic rice and "wild rice". In the past, wild rice, a different genus and species from typical rice, has not been distinguished from typical rice in California's databases. But the distinction is going to be made in the future[5].

3. Salmon and steelhead Evolutionarily Significant Units that may be exposed

There are two Evolutionarily Significant Units (ESUs) of Chinook salmon and one of steelhead that occur in the areas where rice herbicides may be used. These are the Sacramento River Winter-run Chinook salmon ESU, the California Central Valley Spring-run Chinook salmon ESU, and the California Central Valley Steelhead ESU.

<u>Sacramento River Winter-run Chinook salmon ESU</u>

The Sacramento River Winter-run chinook was emergency listed as threatened with critical habitat designated in 1989[6]. This emergency listing provided interim protection and was followed by (1) a proposed rule to list the winter-run on March 20, 1990, (2) a second emergency rule on April 20, 1990, and (3) a formal listing on November 20, 1990[7]. A somewhat expanded critical habitat was proposed in 1992[8] and made final in 1993[9]. In 1994, the winter-run was reclassified as endangered because of significant declines and continued threats[10].

Critical Habitat has been designated to include the Sacramento River from Keswick Dam, Shasta County (river mile 302) to Chipps Island (river mile 0) at the west end of the Sacramento-San Joaquin delta, and then westward through most of the fresh or estuarine waters, north of the Oakland Bay Bridge, to the ocean. Estuarine sloughs in San Pablo and San Francisco bays are excluded[11].

Like other California chinook salmon, the Sacramento River winter-run chinook is included in the "ocean-type" race. This type is more commonly found in coastal streams, but the various chinook ESUs in the Central Valley have much longer migrations inland than do other "ocean-type" chinook. Ocean-type chinook typically have a shorter period of life in fresh water than do "stream-type" chinook. Ocean-type chinook utilize estuarine areas more than the stream-type and also spend their adult lives in ocean waters not far from the coast. Chinook generally spend 1-6 years (more commonly 2-4 years) at sea before returning to their natal stream with a high degree of fidelity[12].

The Sacramento River winter-run chinook used to spawn in the fast, cold headwaters of the Sacramento River and some of its tributaries. Spawning habitat requires clean gravel to construct the redds in which the eggs are laid, adequate flow of oxygenated water, and water temperatures of 5.8-14.1^{o} C (42.5-57.5^{o} F). Since the construction of Shasta and Keswick dams, the passage to the upper Sacramento River and the tributaries has been blocked. However, discharges of cold water from the bottom of the reservoirs has created a spawning habitat for this ESU from below Keswick Dam as far down as the Red Bluff diversion dam. In the 1992 Federal Register Notice designating critical habitat, it was stated that 61% of this ESU spawned between Keswick Dam and Ball's Ferry, 34% between Ball's Ferry and the Red Bluff Diversion Dam, and only 5% below the diversion dam[13].

Newly hatched fry usually move to calmer waters than flows over the redds. As they grow and become stronger swimmers, they move towards deeper and faster water. Smolts in the middle reaches of the Sacramento River are more frequently found in natural, eroding bank habitats with woody debris that provides cover. As they move downstream into estuarine areas, they typically feed in schools in saltmarshes and mudflats, with zooplankton as a primary food in the Delta[14].

<u>California Central Valley Spring-run Chinook salmon ESU</u>

The California Central Valley spring-run chinook salmon ESU was proposed for listing as endangered in 1998[15]. The listing was made final in 1999, but because of increases in the runs, the final designation was as threatened[16]. Critical habitat was designated in 2000[17]. California designated the Sacramento River spring-run as threatened in 1998.

This ESU is most prominent in Butte Creek which contains naturally spawning populations, as do Mill and Deer Creeks. The spawning population in the Sacramento River above Red Bluff diversion dam is declining, as of the listing date in 1999[18]. There is a substantial spawning run in the Feather River, but the genetic integrity of this stock appears to be compromised by hatchery bred fish. Sporadic reports of spawning in Antelope, Cottonwood, and Big Chico creeks are not considered self-sustaining. The listing notice also notes the complete extirpation of the spring run in the San Joaquin River; most of the available spawning habitat is above impassable dams.

As noted above for the Sacramento River winter-run, all California chinook are of the "ocean-type" race. Ocean-type chinook spend less time in freshwater as juveniles. They spend most of their adult life in coastal waters, whereas "stream-type" chinook may undertake extensive ocean migrations. Most adults return to their freshwater, natal streams after 2-4 years at sea (range 1-6 years)[19].

The chinook spring run enters Butte Creek from February through April, and the higher elevation Feather River in May or June, as cited by Yoshiyama[20]. However, according to another *Federal Register* notice, the central valley spring-run chinook enter the Sacramento River from March to July[21]. Spawning occurs in September for this run[22] or occurs from late August through early October with a peak in September[23]. In general, chinook eggs are guarded by the adult for a period of 4-25 days before dying. The eggs hatch 3-5 months after being laid, depending upon temperature, and the juveniles may spend 3 months to two years in freshwater[24]. For the Central Valley spring run, the juveniles emigrate primarily as fry from December to March and may stay in the Sacramento River delta for extended periods[25].

<u>California Central Valley Steelhead ESU</u>
The California Central Valley steelhead ESU was proposed for listing as endangered in 1996[26] and the listing was made final in 1998[27]. Critical habitat was designated in 2000[28]. Critical habitat in the Sacramento River basin includes all of the critical habitat for the winter-run chinook salmon. In addition, a number of tributaries to the Sacramento River are designated to the extent that they are passable: Feather, American and Yuba Rivers, and Battle, Butte, Big Chico, Beegum, Cache, Deer, Mill Antelope, Putah, Stony, and Cottonwood creeks. Also in addition are the San Joaquin River, up to the confluence of the Merced River, and its tributaries to the extent passable. Stanislaus, Calaveras, Consumnes, Merced, Mokelumne, and Tuolumne Rivers are mentioned in table 19 on designated Critical Habitat[29] .

The anadromous steelhead are considered conspecific with the non-anadromous rainbow trout. They may be partly sympatric within the Sacramento River Basin, but they seem to have maintained reproductive isolation. For some ESUs, the steelhead progeny may stay in freshwater and the rainbow progeny may migrate to the ocean.

This steelhead ESU covers both winter and summer run steelhead in the Central Valley. The Service noted that there is effectively one continuous run of steelhead in the upper Sacramento River. The Service also discussed the controversy regarding whether runs are fall or winter, but this distinction is not relevant to our analysis[30].

River entry is from July through May with peaks in September and February. Spawning begins in late December and can extend into April[31]. Eggs are laid in well aerated redds and hatch in 1.5-4 months depending upon temperature. They hatch as ‘alevins’ and stay in the gravel until the yolk sac is absorbed, at which time the ‘fry’ leave the gravel and start to actively feed. Steelhead generally migrate to the ocean after two years in fresh water. Typically, they will reside in marine waters for 2-3 years before returning to their natal stream to spawn. Unlike salmon, steelhead may spawn more than once, but it is unusual for them to spawn more than twice.

4. Risk Assessment

With respect to possible effects on salmon and steelhead, data on aquatic toxicity are relevant. Effects directly on fish are addressed from the fish toxicity data. Indirect effects can theoretically occur through effects on the potential invertebrate food of young salmon and steelhead, and these are addressed from toxicity data on aquatic invertebrates. Because these rice herbicides are used on already cultivated rice fields, they will have no effect on riparian vegetation that could provide shade or cover to salmon and steelhead.

a. Aquatic toxicity

Thiobencarb

Acute toxicity data for thiobencarb are presented in Table 3. For data that met the criteria for use in the RED, the lowest fish 96-hour acute LC50 on technical thiobencarb is a rainbow trout LC50 of 1.2 parts per million (ppm). For the formulated products, the lowest toxicity value for the 10% ai granular product is an LC50 of 0.56 ppm ai on bluegill and for the 84% emulsifiable concentrate is an LC50 of 1.1 ppm ai on rainbow trout. The values for the formulated products are adjusted to reflect the percentage of active ingredient in these products. It appears that the granular product has more toxicity than the technical material. However, it should be noted that intralaboratory variation in different tests with the same species can be two-fold, so it is possible that the different values reflect test variability rather than a higher toxicity for the formulated product, especially since the rainbow trout exhibited slightly less toxicity from the formulated product than from the technical material. Interlaboratory variation is typically somewhat higher than intralaboratory variation and each of these formulations was tested in different laboratories; consequently, OPP does not consider that the degree of variability among these various tests has any significant toxicological relevance.

Additional acute toxicity data were considered in a 1990 review by the California Department of Fish and Game. This report included 29 acute toxicity tests on freshwater fish. These data (other than the several that were independently submitted to EPA) were not validated nor used in the RED. It is not known if the results were adjusted for the percentage of active ingredient. Table 3 presents the results of four of these tests, one each on chinook salmon and steelhead, and the two tests where results indicated more sensitivity, i.e., lower LC50 value, than data that were used in the RED. The other tests demonstrating less sensitivity are not included in Table 3.

Table 3. Aquatic organisms: acute toxicity of thiobencarb to freshwater fish					
Species		% a. i.	LC50 (mg ai/L)	Toxicity Category	
Data cited in Ecological Effects Chapter of RED[32]					
Bluegill	*Lepomis macrochirus*	10[a]	0.56	Highly toxic	
Rainbow trout	*Oncorhynchus mykiss*	10[a]	1.5	Moderately toxic	
Rainbow trout	*Oncorhynchus mykiss*	95.5 (tech)	1.2	Moderately toxic	

Table 3. Aquatic organisms: acute toxicity of thiobencarb to freshwater fish					
Bluegill sunfish	*Lepomis macrochirus*	95.5 (tech)	2.5	Moderately toxic	
Channel catfish	*Ictalurus punctatus*	95.5 (tech)	2.3	Moderately toxic	
Bluegill sunfish	*Lepomis macrochirus*	"tech"	2.6	Moderately toxic	
Carp	*Cyprinus carpio*	"tech"	2.8	Moderately toxic	
Bluegill sunfish	*Lepomis macrochirus*	84.0[b]	1.7	Moderately toxic	
Rainbow trout	*Oncorhynchus mykiss*	84.0[b]	1.1	Moderately toxic	
Channel catfish	*Ictalurus punctatus*	84.0[b]	2.3	Moderately toxic	
Data cited by Harrington (1990)[33]					
Steelhead	*Oncorhynchus mykiss*	85.2[b]	0.79	Highly toxic	
Chinook salmon	*Oncorhynchus tshawytscha*	85.2[b]	0.76	Highly toxic	
Striped bass	*Morone saxatilis*	85.2[b]	0.44	Highly toxic	
White sturgeon	*Acipenser transmontanus*	96.6 (tech)	0.26	Highly toxic	

a. 10G formulation (granular)
b. 8 EC formulation (emulsifiable concentrate)

Aquatic invertebrate toxicity data for technical thiobencarb (Table 4) indicate an LC50 value of 0.1 ppm on *Daphnia magna*. Other tested aquatic invertebrates exhibit less toxicity, as do other formulations with the daphnids. The apple snail LC50 of 1.85 ppm indicates that freshwater molluscs are sensitive as well as arthropods, although the molluscs are less sensitive than *Daphnia*. As with freshwater fish, additional data were reported on these same freshwater invertebrate species by Harrington[34], but these did not show greater sensitivity and were not used in the RED. Toxicity to invertebrates is relevant to concerns for food supply for T&E fish.

Table 4. Aquatic organisms: acute toxicity of thiobencarb to freshwater aquatic invertebrates					
Species		% a. i.	LC50 (mg ai/L)	Toxicity Category	
Daphnid	*Daphnia magna*	10[a]	1.2	Moderately toxic	
Daphnid	*Daphnia magna*	94.4 (tech)	0.10	Highly toxic	
Daphnid	*Daphnia magna*	82.25[b]	0.17	Highly toxic	
Scud	*Gammarus pseudolimnaeus*	95.5 (tech)	0.72	Highly toxic	
Scud	*Gammarus pseudolimnaeus*	85[b]	1.0	Moderately toxic	

Table 4. Aquatic organisms: acute toxicity of thiobencarb to freshwater aquatic invertebrates					
Crayfish	*Cambarus clarkii*	95.5 (tech)	2.0	Moderately toxic	
Apple snail	*Pomacea aludosa*	85[b]	1.85	Moderately toxic	

a. 10G formulation
b. 8 EC formulation

Data on chronic toxicity of thiobencarb are presented in Table 5. There is a significant disparity in the data for *Daphnia*. Since both tests have been considered valid, I have used the lowest endpoint. Data have been requested on toxicity for fish early-life stage, but these data are not yet available. However, Harrington did report some chronic toxicity data for chinook salmon in tests that were not standard and therefore cannot be directly compared with data in Table 5. These include (1) a 60-day 'eggs-to-fry' LC50 test with Chinook salmon using the 85.2% 8EC formulation, where the 60-day LC50 was 200 ppb and (2) a 90-day 'eggs-to-fry' test with Chinook salmon using the 85.2% 8EC formulation, where the no-observed-effect-concentration (NOEC) was 28 ppb and the lowest-observed-effect-concentration (LOEC) was 49 ppb, based on survival and growth.

Table 5. Aquatic organisms: chronic toxicity of thiobencarb to freshwater fish and aquatic invertebrates					
Species		% a. i.	NOEC (ppb)	LOEC (ppb)	MATC (ppb)[a]
Daphnid	*Daphnia magna*	95.2-95.9 (tech)	1.0	3.0	1.7
Daphnid	*Daphnia magna*	96.9 (tech)	48	90	66
fish			no data	test requested	

a. The MATC is the "maximum allowable toxicant concentration" which is the geometric mean of the NOEC and LOEC.

There are abundant data relating to health effects and terrestrial uses, and these can be found on pages 5-7 and 37-38 of the RED, even though they are not herein considered relevant to salmon and steelhead. In summary, thiobencarb is considered slightly to practically non-toxic to birds and mammals on an acute basis. On a chronic basis, conservative NOECs are 100 ppm dietary for birds and 20 ppm dietary for mammals.

<u>Molinate</u>

The ecological effects risk assessment for freshwater fish noted a large discrepancy among the toxicity data (Table 6). Two studies conducted at the Columbia National Fisheries Laboratory showed LC50 values of 0.21 ppm for rainbow trout and 0.32 ppm for bluegill. These values are one to two orders of magnitude below most of the other LC50 values. The basis for the discrepancy is not apparent as is discussed in more detail in Appendix C (p8) of the Ecological Review[35]. It was noted in Appendix F (p9) that these acute values are also below the NOEC of 0.39 ppm for a subchronic early-life-stage test[36]. Tests on the formulated product are consistent with those on the active ingredient, indicating that other ingredients than active ones provide no meaningful addition to the toxicity of the active ingredient. The ecological effects chapter of the molinate RED did include the acute data reported by Harrington.

Table 6. Aquatic organisms: acute toxicity of molinate to freshwater fish

Species		% a. i.	LC50 (mg ai/L)	Toxicity Category	
Rainbow trout	*Oncorhynchus mykiss*	96.8 (tech)	20	Slightly toxic	
Rainbow trout	*Oncorhynchus mykiss*	98.6 (tech)	0.21	Highly toxic	
Bluegill sunfish	*Lepomis macrochirus*	96.8 (tech)	23.1	Slightly toxic	
Rainbow trout	*Oncorhynchus mykiss*	97.8 (tech)	1.3	Moderately toxic	
Bluegill sunfish	*Lepomis macrochirus*	98.6 (tech)	0.32	Highly toxic	
Carp	*Cyprinus carpio*	"tech"	2.8	Moderately toxic	
Bluegill sunfish	*Lepomis macrochirus*	99 (tech)	18.8	Slightly toxic	
Rainbow trout	*Oncorhynchus mykiss*	99 (tech)	6.97	Moderately toxic	
Bluegill sunfish	*Lepomis macrochirus*	97.8 (tech)	29	Moderately toxic	
Catfish	(unknown spp)	"tech"	13.0	Slightly toxic	
Fathead minnow	*Pimephales promelas*	99 (tech)	26.0	Slightly toxic	
Carp	*Cyprinus carpio*	"tech"	42.8	Slightly toxic	
Rainbow trout	*Oncorhynchus mykiss*	90.3[a]	19.5 (17.6 mg ai/l)	Slightly toxic	
Steelhead	*Oncorhynchus mykiss*	90.3[a]	14	Slightly toxic	
Chinook	*Oncorhynchus tshawytscha*	90.3[a]	13	Slightly toxic	
Bluegill sunfish	*Lepomis macrochirus*	90.3[a]	24 (21.7 mg ai/l)	Slightly toxic	
Channel catfish	*Ictalurus punctatus*	90.3[a]	34	Slightly toxic	

Table 6. Aquatic organisms: acute toxicity of molinate to freshwater fish					
Striped bass	*Morone saxatilis*	90.3[a]	8.1	Moderately toxic	
Mosquito fish	*Gambusia affinis*	71[b]	26 (18 mg ai/l)	Slightly toxic	
Goldfish	*Carrasius auratus*	97.8 (tech)	30	Slightly toxic	

a. Ordram 8E
b. Ordram 6E

Toxicity data on aquatic invertebrates (Table 7) are comparable to those for fish. The lowest LC50 value is 0.3 ppm in a non-standard test and 0.34 ppm in a standard test.

Table 7. Aquatic organisms: acute toxicity of molinate to freshwater aquatic invertebrates					
Species		% a. i.	LC50 (mg ai/L)	Toxicity Category	
Daphnid	*Daphnia magna*	tech	19.4 (48 hr)	Slightly toxic	
Daphnid	*Daphnia magna*	tech	0.70 (26 hr)	Highly toxic	
Daphnid	*Daphnia magna*	91.2[a]	4.7 (48 hr)	Highly toxic	
Stonefly	*Pteronarcys sp.*	98.6 (tech)	0.34 (96 hr)	Highly toxic	
Scud	*Gammarus lacustris*	98.6 (tech)	4.5 (96 hr)	Moderately toxic	
Cladoceran	*Moina australiensis*	tech	0.30 (8 day)	Moderately toxic	

a. Ordram 8E

The available data on subchronic toxicity (Table 8) indicate that longer exposures result in only small increases, if any, in toxicity. The lowest NOECS were found for carp. Finlayson and Faggella[37] conducted a 28 day test on carp and found the no effect level, based on carp hematocrit values, at 90 ppb. They also reanalyzed a Japanese 21-day study on carp that had an even lower no-effect level of 32 ppb, but details on this Japanese study are not available.

Table 8. Aquatic organisms: subchronic toxicity of molinate to freshwater fish and aquatic invertebrates						
Species		duration	% a. i.	LC50 (ppb)	NOEC (ppb)	LOEC (ppb)
Carp	*Cyprinus carpio*	28 d	90.3[a]	210	90	130
Carp	*Cyprinus carpio*	18 d	unk	180	32	
Channel catfish	*Ictalurus punctatus*		90.9[a]	6100	880	1570
Channel catfish	*Ictalurus punctatus*	8 d	90.3[a]	>8600	1700	2600

Table 8. Aquatic organisms: subchronic toxicity of molinate to freshwater fish and aquatic invertebrates						
Bluegill sunfish	*Lepomis macrochirus*	30 d	90.9[a]	>6050	6050	

a. Ordram 8E

Table 9 presents chronic toxicity data for molinate. As noted above, the chronic NOEC for rainbow trout was higher than the acute LC50 value for rainbow trout in Table 6. As with thiobencarb, Harrington reported one chronic toxicity test for chinook salmon in a test with the 90.3% 8EC formulation of molinate that was not standard and therefore cannot be directly compared with data in Table 9. In this 90-day 'eggs-to-fry' test with Chinook salmon, the NOEC was 420 ppb and the LOEC was 730 ppb, based on survival and growth. A chronic LC50 value, presumably for the whole 90-day period, was calculated at 740 ppb.

Table 9. Aquatic organisms: chronic toxicity of molinate to freshwater fish and aquatic invertebrates

Species		duration	% a. i.	NOEC (ppb)	LOEC (ppb)	MATC (ppb)
Daphnid	*Daphnia magna*	21 d	97.5	380	900	590
Cladoceran	*Moina australiensis*	8 d	tech	110	290	180
Rainbow trout	*Oncorhynchus mykiss*	30 d	99	390	830	570

There are abundant data relating to health effects and terrestrial uses of molinate. These are considered in detail in the Toxicology Chapter on OPP's website[38]. In summary, molinate is considered to be of low acute toxicity to mammals from oral, inhalation, or dermal exposure. On a subchronic or chronic basis, molinate has been found to cause delayed neurotoxicity in dogs at dietary concentrations as low as 1 mk/kg/day; a NOEC of 7 ppm (0.3-0.4 mg/kg/day) dietary was established for neurotoxicity in rats. In hens, the NOEC for neurotoxicity was 200 mg/kg from a single oral dose. In longer term mouse and rat studies, conservative NOECs were 10 ppm dietary for effects on mouse testes, and 100 ppm for other chronic effects. The reproductive effects NOEC in rats was 6 ppm dietary in a 2-year study. Molinate is considered a potential carcinogen.

Birds were not affected at the highest doses in an avian acute oral study, and there was no molinate-related mortality in avian dietary tests. Molinate is considered "practically non-toxic" to birds on an acute basis. Based on effects noted in mammalian studies, avian reproduction tests are now required.

Combined toxicity

Finlayson and Faggella[39] studied the aquatic acute toxicity of a thiobencarb-molinate mixture comprised of 1:1 LC50-value ratios to determine if combined toxicity was additive, antagonistic, or synergistic. The results for the three test species, steelhead, chinook salmon, and channel catfish showed that the combined toxicity was additive.

b. Environmental fate and transport

In the environmental fate assessment portion of the thiobencarb RED, it was stated (p51), "Thiobencarb is generally nonpersistent in the water column but moderately persistent in soils and sediments." The aqueous photolysis laboratory study results indicate a 12-day half life which was used in the risk assessment (p52). Actual residue levels in California indicated half-lives of 8.7 days in a directed study and 4.5 days from a literature review (p53). Thiobencarb does not bioconcentrate to any great extent, and depuration is quite rapid[40].

In the environmental fate assessment portion of the molinate review, it was found that molinate is stable in the laboratory to photolysis and hydrolysis. Field dissipation from rice water is more rapid than would be estimated from laboratory data; this dissipation is apparently due to volatilization and to binding to the clay soil in the rice fields. Molinate is considered mobile, but the clay soils of California rice fields are considered relatively impermeable to any leaching. Molinate is not expected to bioconcentrate[41].

Environmental fate and transport data can be used to model concentrations in aquatic environments. There is no modeling scenario available to address rice, although one has been developed and is under review. A model would not apply very well to California because of the permit conditions developed by the county agricultural commissioners in accordance with Section 14007 of the California Food and Agricultural Code and Section 6432, Title 3 of the California Code of Regulations. With respect to T&E salmon and steelhead, these rules primarily relate to holding of treated water following application of pesticides. At the present time, rice water treated with granular thiobencarb and molinate must be held for 28 and 30 days, respectively, before being discharged from the fields. For rice water treated with liquid applications of thiobencarb needs to be held 19 days before discharge from the fields. Under certain conditions, emergency permission can be obtained to prematurely discharge the water from the fields into drains or other holding areas, but not into natural waters.

c. Levels of concern for aquatic risk

Based upon OPP's criteria for risks to endangered and threatened aquatic animals, concerns would exist if the aquatic acute LC50 for fish exceeded 0.05x the EEC for direct acute risk. For acute risks to the aquatic invertebrate food supply for T&E fish, the criteria of concern is when the aquatic invertebrate acute LC50 exceeds 0.5x the EEC, and for chronic effects, the criteria are exceeded if the chronic NOEC exceeds the EEC.

For thiobencarb, the lowest acute fish value was 0.26 ppm for the technical material and white sturgeon. The EEC concern level on this basis would be 13 ppb. The lowest aquatic invertebrate LC50 was 100 ppb, which yields a concern if the EEC exceeded 50 ppb. There is no "typical" chronic fish data for thiobencarb; however the 90-day chinook salmon NOEC was 28 ppb; the aquatic invertebrate NOEL is 1 ppb.

For molinate, the lowest acute fish value was 0.21 ppm for the technical molinate and rainbow trout. The EEC concern level on this basis would be 10.5 ppb. The lowest aquatic invertebrate LC50 was 300 ppb, which yields a concern if the EEC exceeded 150 ppb. The chronic fish NOEL is 390 ppb for rainbow trout.

d. Discussion of residue measurements relative to concern levels

USGS monitoring data have been developed for the San Joaquin-Tulare Basin[42] and for the Sacramento River Basin[43]. In the San Joaquin-Tulare basin the highest molinate residues from 1992-1995 were ~7ppb (as interpreted from graph) for molinate and ~0.9 ppb for thiobencarb. These residue levels are below our criteria of concern. In the Sacramento River Basin, the highest molinate residues from 1994 to 1998 were 19 ppb and the highest thiobencarb residues were 7 ppb, again as interpreted from a graph. However, these residues were found in the Colusa Basin drain which drains an agricultural area that includes much of the Glenn and Colusa county rice. Concentrations in the Sacramento River at Freeport did not exceed 2 ppb for molinate; no data were presented for thiobencarb, but Domagalski et al[44] stated that "...concentrations [of rice pesticides] ...always were very low in the Sacramento River."

Following a variety of fish kills in the 1970s and 1980s, water-holding requirements were developed to avoid levels of pesticides that could be harmful to fish, especially in natural waters such as the Sacramento River, but even applying to some degree in the agricultural drains. California's Central Valley Water Quality Control Board has set "performance goals" to reduce molinate residues to below 10 ppb and thiobencarb levels to below 1.5 ppb even in the agricultural drains. While these are not always achieved in the agricultural drains themselves, the levels in the Sacramento River have consistently been below these levels for 10 years, except for one 1.6 ppb measurement of thiobencarb this year[45]. The peak residue in the Sacramento River for molinate, which still met the performance goals, was also this year on the same day as occurred for thiobencarb, immediately following a significant storm event.

Water is regularly sampled by the state at several locations near Sacramento. In weekly monitoring in the Sacramento River during the rice herbicide season, residues in 2001 peaked at 2.12 ppb for molinate and 0.59 ppb for thiobencarb. Sampling sites were at the "Village Marina", upstream from Sacramento, and at the water intakes for Sacramento and West Sacramento.

The Colusa Basin drain does flow into the Sacramento River. There are occasional exceedances of the Water Quality Board's performance goals in this drain, but the more appropriate habitat to be considered in this area is the Sacramento River itself. Over the ten years of substantial monitoring of thiobencarb and molinate residues in the Sacramento River, residues have never exceeded the acute criteria of concern for fish nor for their invertebrate food supply. During this period, molinate residues have never exceeded the criteria of concern for chronic effects. Data are lacking on the chronic effects of thiobencarb to fish, but comparing the acute and chronic invertebrate data for thiobencarb with the fish acute data suggests that chronic toxicity data would not result in a chronic risk concern. Perhaps more importantly, thiobencarb and molinate are applied at a single time of the year in April and May. This, in combination with the flowing water of the Sacramento River, should preclude any chronic exposure to salmon and steelhead.

There are anecdotal reports of adult salmon going up into the Colusa Basin Drain in the fall[46]. Because of the timing of herbicide applications to rice in the spring, these adult fish would not be exposed to molinate or thiobencarb concentrations of concern. Other anecdotal reports[47] indicate that juvenile salmon and steelhead, approximately 2-3 inches long, may go up into this drain during various times of the year. In May and the first half of June, when molinate and thiobencarb are being used, the spring and fall runs may be represented. It appears that the winter-run chinook are beginning to move down the Sacramento River past the drain towards the end of June, but this is after the peak use and when peak residues have been found.

Measurement of residues in the Colusa Basin Drain have been taken by both USGS and the state. In 2001, the targeted performance goals set by the Central Valley Water Quality Control Board were exceeded for both molinate and thiobencarb. The thiobencarb residues were below our criterion of concern, but the molinate residues in the drain were measured at 12.1 and 12.7 ppb, which slightly exceeds our criterion of 10.5 ppb. In 2000, thiobencarb residues were again below our criterion, but molinate residues were above, being measured as high as 22 ppb. During the USGS monitoring reported for 1996-1998[48], the maximum thiobencarb residues were 4.4 ppb (median 0.026 ppb) and the maximum molinate residues were 19 ppb (median 0.1 ppb).

All of these residue data indicate no concern at all for thiobencarb. Although this agricultural drain does occasionally have molinate residues above our criteria, there is probably no concern for several reasons. First, the Colusa Basin drain is not the kind of habitat likely to be used by salmon and steelhead except for some strays. It is effectively a leveed ditch; it is large, deep, and slow and contains no spawning habitat. Second, the concern levels for molinate are based upon two tests that demonstrated toxicity levels two orders of magnitude more sensitive than all of the other molinate acute data; these acute data were even lower than chronic test data for molinate on both rainbow trout and chinook salmon. In addition, our criteria of concern for aquatic organisms are quite conservative.

5. Conclusion

Based upon the data and other information available to me, I conclude that the use of thiobencarb and molinate, as registered for use on rice in California, is not likely to adversely affect the Sacramento River winter-run chinook salmon, the California Central Valley Spring-run chinook salmon, or the California Central Valley steelhead.. This conclusion is based primarily on the very low residue levels of thiobencarb and molinate that have been found over the last ten years in the natural waters where these salmon and steelhead occur, and a comparison of these residues with the fish toxicity information. A very significant factor in this conclusion is the marked effect that the mandatory water-holding requirements have on the exposure of fish in the Sacramento River and the San Joaquin River and their tributaries.

I further conclude that there will be no effect on any other listed salmon or steelhead because thiobencarb and molinate are not used in areas where these other salmon and steelhead occur.

6. Summary of relevant factors

1. There are 500,000 acres of rice grown in California, mostly in the Sacramento River Basin.
2. Molinate is used on about half the rice acreage and thiobencarb is used on about half the rice acreage. There is probably substantial overlap in the acres treated with both.
3. Technical molinate is considered slightly to highly toxic to fish on an acute basis. The emulsifiable concentrate is considered slightly to moderately toxic. The lowest LC50 is 210 ppb.
4. Technical thiobencarb and the emulsifiable concentrate formulation are moderately toxic to fish on an acute basis. The granular thiobencarb is considered highly toxic to fish. The lowest LC50 is 260 ppb.
5. There is not a valid exposure modeling scenario for rice. Based upon the toxicity values and OPP's endangered species concern levels, there would be concerns if the environmental concentration exceeded 13 ppb for thiobencarb or 10.5 ppb for molinate.
   A. For thiobencarb, the lowest acute fish value was 0.26 ppm for the technical material and white sturgeon. The EEC concern level on this basis would be 13 ppb. The lowest aquatic invertebrate LC50 was 100 ppb, which yield a concern for invertebrate food supply if the EEC exceeded 50 ppb. The chronic fish toxicity data in a non-standard test for thiobencarb show a NOEC of 28 ppb for chinook salmon; the aquatic invertebrate NOEL is 1 ppb.
   B. For molinate, the lowest fish acute value was 0.21 ppm for the technical product. The EEC concern level on this basis would be 10.5 ppb. The lowest aquatic invertebrate LC50 was 300 ppb, which yield a concern for invertebrate food supply if the EEC exceeded 150 ppb. The no effect level for chronic effects on fish was 390 ppb.
6. Maximum residues found in natural waters providing habitat for salmon and steelhead have been consistently below levels of concern for acute toxicity directly to fish or indirectly to their invertebrate food supply.
7. Typical residues found in natural waters providing habitat for salmon and steelhead have been consistently below levels of concern for chronic toxicity.
8. Maximum residues of molinate may exceed our criteria of concern in agricultural drains, but use of the drains is very likely to be quite low and our risk assessment for molinate is based on very conservative toxicity values.

Endnotes

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